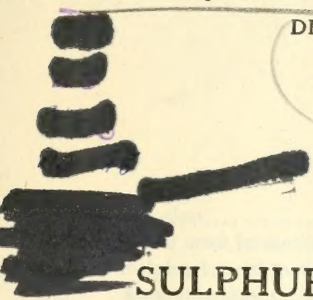


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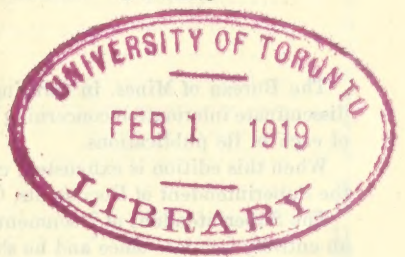
Technical Paper 198

DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, SECRETARY
BUREAU OF MINES
VAN. H. MANNING, DIRECTOR



SULPHUR DIOXIDE METHOD FOR DETERMINING COPPER MINERALS IN PARTLY OXIDIZED ORES

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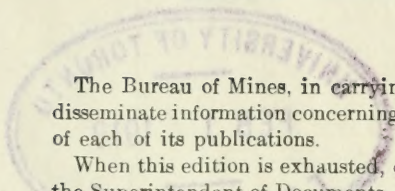
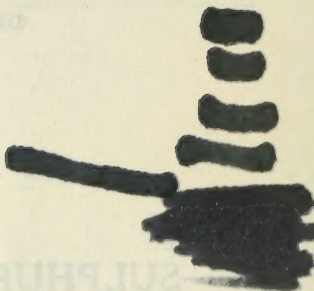
CHARLES E. VAN BARNEVELD
AND
EDMUND S. LEAVER

ENGIN STORAGE



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1918

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
SULPHUR DIOXIDE METHOD FOR
DETERMINING COPPER MINERALS
IN PARTLY OXIDIZED ORES



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TABLES

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Figure 1. Apparatus for preparation of sulphur dioxide solution.....

SULPHUR DIOXIDE METHOD FOR DETERMINING COPPER MINERALS IN PARTLY OXIDIZED ORES.

By CHARLES E. VAN BARNEVELD and EDMUND S. LEAVER.

INTRODUCTION.

Milling practice at the porphyry copper mines of the Southwest is in a transition stage because of the rapid changes following the introduction of flotation. Among the several problems that are receiving earnest attention from the operating companies is the recovery of the copper minerals forming the complex ores of the oxidation zone of the deposits.

This problem is under investigation at the Tucson mining experiment station of the Federal Bureau of Mines. A survey of the status of present laboratory practice brought out the need of a correct and rapid method for the selective determination of the quantity of copper in the sulphide form, on the one hand, and of that in the form of combined oxides, carbonates, silicates, and native or metallic copper, on the other hand, in partly oxidized ores and in mill products from these ores.^a Such a method is necessary for control determinations on flotation mills treating sulphide ores and also on lixiviation works using either acids or alkalines as the active solvent for the copper in oxidized and in silicate form. For convenience such copper is termed "oxidized copper."

SOURCES OF ERROR IN METHODS IN USE.

The methods in common use for the selective determination of copper minerals are the sulphuric acid method and the ammonia method. Both are unsatisfactory.

SULPHURIC ACID METHOD.

The sulphuric acid method, in which a 5 per cent solution of cold sulphuric acid is used to dissolve all the oxidized copper, is unreliable for several reasons. A certain amount of metallic iron (ranging from one-tenth to one-half of 1 per cent) is nearly always present in the sample, introduced by the various crushing (mill) and pulverizing

^a The analytical work in connection with the development of the method described in this paper was done at the Tucson station by G. E. Postma, junior chemist.

(laboratory) processes. This metallic iron precipitates more or less metallic copper from the copper sulphate solution formed by leaching with dilute sulphuric acid, thus giving correspondingly low oxidized-copper returns. Another source of error in the same direction is the fact that dilute sulphuric acid dissolves only one-half the copper present as cuprite (Cu_2O). A serious source of error in the opposite direction, making for high oxidized returns, is the fact that chalcopyrite, bornite, and chalcocite are more or less soluble in dilute sulphuric acid (see Table 1). Hence, more or less copper in sulphide form is reported as oxidized copper. It sometimes happens that the plus error due to solution of some of the copper in sulphide form is largely compensated by the minus error due to partial solution of cuprite and to deposition of copper on metallic iron. The majority of the ores tested by the writers show high oxidized and low sulphide returns, and check samples show considerable variation.

The results of tests with chalcocite and chalcopyrite, showing the solubility of the copper content in different reagents, are presented in Table 1 following:

TABLE 1.—*Results of leaching chalcocite and chalcopyrite with 5 per cent solutions of different reagents.*

[The mixtures were agitated 2 hours on a bottle-rolling machine. Five grams of pure mineral was used for each of the mesh sizes indicated.]

Mesh.	Proportion of copper content leached from—					
	Chalcocite with solution of—			Chalcopyrite with solution of—		
	Sulphuric acid.	Ammonia and ammonium carbonate.	Sulphur dioxide.	Sulphuric acid.	Ammonia and ammonium carbonate.	Sulphur dioxide.
	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>	
20 to 40.....	0.11	3.87	None.....	0.03	0.12	None.
40 to 65.....	.28	7.50	...do.....	.04	.18	Do.
65 to 100.....	.36	14.10	...do.....	.06	.21	Do.
100 to 150.....	.60	16.50	...do.....	.15	.32	Do.
150 to 200.....	.82	17.13	...do.....	.17	.45	Do.
200.....	2.07	22.70	...do.....	.56	.93	Do.

All copper-sulphide minerals are coated with an oxidized film. Therefore in the experiments, in order to remove this film, a preliminary treatment was given with the reagent to be tested. A first washing with sulphur dioxide invariably showed appreciable traces of copper, but subsequent treatments showed no soluble copper whatever, whereas, with sulphuric acid successive treatments of the same sample with the same strength of acid for the same period show a practically constant rate of solution. A picked specimen of so-called pure chalcocite was ground in a porcelain mortar to 100 mesh. A 2-gram sample was treated for 2 hours four successive times in a

bottle-roll machine with 100 c. c. of 4 per cent sulphuric acid. The first treatment dissolved 0.0132 grams of copper (0.65 per cent) and the subsequent treatments dissolved 0.0113 grams (0.56 per cent), 0.0111 grams (0.55 per cent) and 0.0106 grams (0.53 per cent). That the first treatment dissolved the most copper was doubtless due to the presence of an oxidized film.

AMMONIA METHOD.

The ammonia method, in which a 5 per cent solution of either ammonia or of ammonia and ammonium carbonate is used to dissolve the oxidized copper, is even more unreliable than the sulphuric acid method. The results in Table 1 show that both chalcopyrite and chalcocite when pulverized are decidedly soluble in solutions of ammonia and ammonium carbonate, the finer the material is ground the greater is the degree of solubility. On the other hand, complete solution of the oxidized copper is rarely attained. This defect is most noticeable in ores having a siliceous gangue and in ores carrying chrysocolla. The solvent gelatinizes the silica and it appears that the formation of this gelatinous, spongy mass prevents complete decomposition of some of the copper mineral, in addition to holding dissolved copper during filtration.

SODIUM TARTRATE METHOD.

While the investigation at the Tuscon station was in progress, an improved method was developed by H. D. Hunt and R. V. Thurston, of the research laboratory of the Miami Copper Co. This method was brought to the writers' attention after the completion of their own work on the sulphur dioxide method described in this paper. A description of the Hunt and Thurston method, which may be called the sodium-tartrate method, has been published in the September, 1917, issue of the Colorado School of Mines Magazine.* The procedure is essentially as follows:

PROCEDURE.

Place 2 grams of pulp in a beaker, add 20 c. c. of a solution of caustic soda-sodium tartrate, and boil the mixture gently 5 to 10 minutes with occasional shaking of the beaker. To the hot mixture add 25 c. c. of a 20 per cent solution of ammonium sulphate; heat for 10 minutes. Filter; wash several times with a hot solution of ammonium hydroxide and ammonium sulphate, and finish the washing with hot water. Neutralize the filtrate with sulphuric acid and add $2\frac{1}{2}$ c. c. of concentrated sulphuric acid, then add $2\frac{1}{2}$ c. c. of concentrated nitric acid. The filtrate is now ready for electrolysis.

* Hunt, H. D., and Thurston, R. V., The determination of oxidized copper in ores: Colorado School of Mines Mag., vol. 7, September, 1917, pp. 157-158.

The first treatment with the solution of caustic soda and sodium tartrate effects complete and rapid solution of the azurite, malachite, and melaconite, and partial solution of the cuprite. The rest of the cuprite is dissolved later. The chrysocolla also goes into solution. Care must be taken not to boil to dryness or to a small volume. The reagent must be of sufficient strength to redissolve the copper hydroxide first formed by the action of the solution on the oxidized copper minerals in the sample. The ammonium sulphate solution has a twofold function. It converts the excess sodium hydrate into sodium sulphate and it forms ammonium hydroxide which in turn dissolves any remaining cuprite.

SOLUTIONS REQUIRED.

The following stock solutions are required: Sodium hydrate-sodium tartrate solution, consisting of 100 grams of sodium hydrate and 50 grams of sodium tartrate dissolved in 1,000 c. c. of distilled water; ammonium sulphate solution, consisting of 250 grams of ammonium sulphate in 1,000 c. c. of distilled water; and ammonia-ammonium sulphate solution for washing, prepared by adding 100 c. c. of ammonium hydroxide and 100 grams of ammonium sulphate to 1,000 c. c. of distilled water.

POSSIBLE SOURCES OF ERROR.

In testing this method, the writers found that it gives fairly satisfactory results with the low-grade porphyry ores for which it was developed. The method is, however, subject to two well-defined inaccuracies.

One of these arises from the fact that chalcocite is decidedly soluble in ammonia. Washing with hot solution of ammonia and ammonium sulphate unquestionably dissolves more or less copper in the form of chalcocite from the mass on the filter paper. Several tests were made of 2-gram samples containing 3 to 4 per cent of oxidized material and varying proportions of chalcocite. Mixtures containing 8, 16, and 24 per cent copper as chalcocite respectively showed 0.18, 0.33, and 0.45 per cent dissolved in washing and erroneously reported as excess oxidized copper.

Another source of inaccuracy, as regards ores containing chrysocolla, results from the difficulty of washing all the dissolved copper from the gelatinized spongy mass on the filter paper. Mixtures containing $2\frac{1}{2}$ to 3 per cent copper as chrysocolla showed losses ranging from 0.05 to 0.1 per cent; and mixtures containing 5 and $7\frac{1}{2}$ per cent copper in this form respectively showed losses of 0.33 and 1.42 per cent. These errors tend to balance each other for ores containing

both chalcocite and chrysocolla in small amounts. In analyses of ores containing less than 5 per cent copper, the resultant error (see Table 2, p. 8) is not serious.

SULPHUR DIOXIDE METHOD.

The experiments with the sulphur dioxide method were made with the following requirements in mind:

1. The method must be applicable to a wide range of ores, and must be thoroughly reliable and rapid.

2. Copper sulphides, especially the more easily decomposed chalcocite, must not be affected by the reagent used.

3. Metallic iron must not affect the determination.

The method evolved is based on a large number of experiments, which show conclusively that cuprite, melaconite, malachite, azurite, and chrysocolla, when finely pulverized, are readily and completely soluble in sulphur dioxide solution. As certain copper silicates resist the action of strong, hot sulphuric acid, a careful investigation was made of the action of sulphur dioxide. Specimens of chrysocolla from various sources and selected samples of copper silicates representing all the large mines in the Southwest were treated with sulphur dioxide solution and the copper in every sample completely dissolved: not a trace of copper could be found in the residue. Any finely divided metallic copper present in the sample is likewise dissolved. Copper sulphides are not attacked, no matter how finely pulverized the mineral may be nor how long the time of contact. The three essential features of the method are as follows: (1) Fine pulverization to free completely the particles of copper minerals from the gangue; (2) keeping the powdered mineral in suspension by shaking or rolling during the lixiviation or solution period; (3) using sulphur dioxide solution (sulphurous acid) and not sulphur dioxide gas.

PROCEDURE.

The procedure in the sulphur dioxide method is as follows:

Place 2 grams of pulp ground to a fineness of 100 to 150 mesh in a bottle, add 100 c. c. of a 3 per cent solution of sulphur dioxide. Seal the bottle and agitate by rolling one-half to two hours. Filter: wash the residue with sulphur dioxide solution: add the washings to the filtrate, which will contain in solution all oxides, carbonates, and silicates of copper and all metallic copper. Add 5 to 10 c. c. of nitric acid. Boil down to 20 c. c. Dilute with distilled water to 150 c. c. and determine the copper by the electrolytic method in the usual way.

The residue from filtration contains the unaltered and undissolved copper sulphides. In the experimental work the copper present as sulphide was separately determined in order to check the determina-

tion of oxidized copper. Ordinarily this step would not be necessary. In analyses of the low-grade porphyry copper ores of the Southwest, the sulphides may be readily decomposed and all the copper dissolved by proceeding as follows: To the residue, add 5 c. c. of

sulphuric acid and 10 c. c. of nitric acid and boil until dense white fumes appear. Add 5 c. c. of nitric acid and dilute with distilled water to 150 c. c. Determine the copper by the electrolytic method. This method of determining copper in the residue is not suited for heavy sulphide ores containing interfering bases, and for such ores standard methods should be used.

PREPARATION OF SOLUTION.

Although sulphur dioxide solution (sulphurous acid) may be readily purchased, it is decidedly unstable; hence the solution should be prepared in the laboratory as needed. Small quantities are easily made by adding moderately strong sulphuric acid to scrap copper tinned on one side; the resulting sulphur dioxide gas is absorbed in water. For continuous work it is better to purchase liquid sulphur

dioxide in steel cylinders and drums, which are obtainable in sizes ranging from 6-pound to 200-pound capacity. In the first experiments at the Tucson station the sulphuric dioxide gas was introduced directly into the bottle containing the water and pulp. Much loss of gas resulted and the procedure was otherwise unsatisfactory.

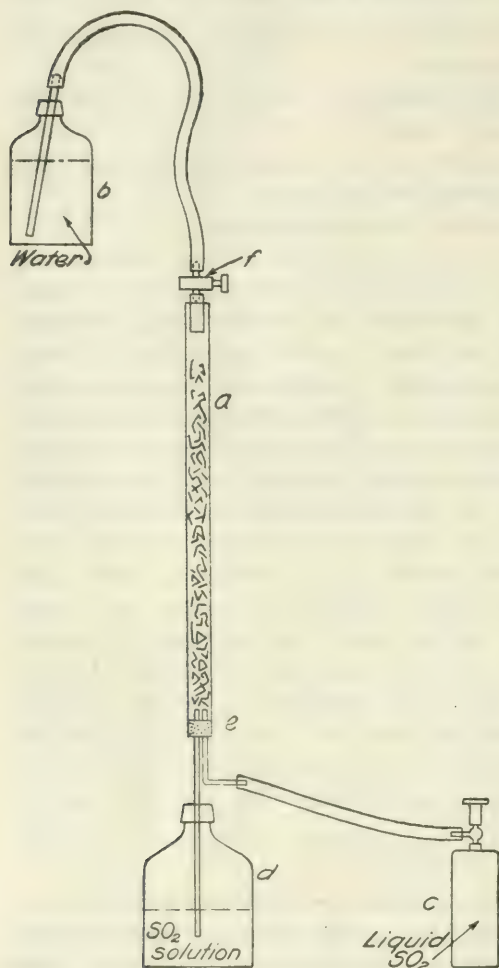


FIGURE 1.—Apparatus for preparation of sulphur dioxide solution; a, absorption tower; b, distilled water bottle; c, container for liquid sulphur dioxide; d, bottle for sulphur dioxide solution; e, plug of sealing wax.

Later the simple apparatus shown in figure 1 was evolved. A vertical absorption tower *a*, 42 inches long, made of $\frac{3}{4}$ -inch to 1-inch glass tubing and filled with broken hard-burned fire clay, is set between two glass bottles *b* and *d*, of 3 to 5 gallons' capacity, the bottle *b* being placed about 5 feet above the other bottle. This tower is open at the top and sealed at the bottom with a plug of sealing wax *e*, through which two small glass tubes extend. The upper bottle *b* contains distilled water, which is siphoned into the upper end of the absorption tower, the flow being regulated by a stopcock *f*. A cylinder *c* (capacity 6 to 50 pounds), containing liquid sulphur dioxide, is connected to one of the glass tubes extending into the absorption tower. On opening the valve of this cylinder the liquid sulphur dioxide issuing from the valve is gasified by the reduction in pressure and passes into the tower, where it is absorbed by the water from bottle *b*, converted into sulphur dioxide solution of the desired strength and caught in the stock bottle *d*.

This apparatus gives entire satisfaction. With little attention, a 3 per cent solution of sulphur dioxide may be produced at the rate of 3 liters per hour. The cylinder containing liquid sulphur dioxide indicated in the sketch may be replaced with an SO₂ gas generator.

STRENGTH OF SOLUTION AND TIME OF CONTACT.

Considerable variation as regards strength of solution and time of contact will be necessary in treating different ores from different localities. In general, for porphyry copper ores a solution containing 3 per cent sulphur dioxide should be used. With some ores much weaker solutions, containing as low as 0.75 per cent sulphur dioxide, will do the work. Merely introducing the pulp into the solution, shaking the bottle for a few minutes, and letting it stand, will not dissolve the copper; constant agitation is essential. For a small number of tests a bottle-agitating machine will give satisfactory results. For analytical work, where large numbers of samples are run, as in a mine laboratory, a bottle-rolling machine will be found more satisfactory, not only for this purpose, but for all solutions requiring constant agitation. The time of contact necessary to completely dissolve the oxidized copper minerals was found to vary from one-half to two hours. Most of the ores and products tested gave complete recovery in half an hour, and the most refractory ores yielded in less than two hours.

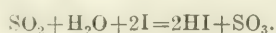
TESTING STRENGTH OF SOLUTION.

To determine the strength of the sulphur dioxide solution, the following adaptation of a well-known reaction is recommended. It is based on the fact that introducing either weak or concentrated sulphurous acid into a solution of iodine will result in the complete oxidation of the sulphur dioxide.

Prepare an iodine solution by dissolving 16.8 grams of potassium iodide in distilled water, adding 8.4 grams pure resublimed iodine, and shaking until the iodine is completely dissolved. The more concentrated the potassium iodide solution the more readily will the iodine dissolve. Bring the solution to proper strength by adding enough distilled water to make a volume of 1 liter. Then standardize the solution by the thiosulphate method, using starch indicator.

The determination is made as follows: To a measured quantity of standard iodine solution add slowly, with constant stirring, the proper volume of sulphur dioxide solution. So regulate the volume of iodine solution used that the mixture always contains a decided excess of iodine over the quantity required to oxidize the sulphur dioxide being added. An excess of sulphur dioxide causes the solution to clear and to lose its dark-red color. If an excess of sulphur dioxide is added, the determination is spoiled, and the test should be repeated with fresh sulphur dioxide solution and a larger quantity of iodine solution. Thus, there is a relation between the strength and quantity of sulphur dioxide solution and the quantity of standard iodine solution.

In general, when the solution to be standardized varies in strength from 1 to 3 per cent sulphur dioxide, add 1 c. c. of this solution to 20 c. c. of standard iodine solution. When the sulphur dioxide solution is appreciably below 1 per cent in strength add a larger quantity of it. The mixture is then titrated by the thiosulphate method to determine the quantity of iodine remaining in the mixture. The difference between this quantity and the total quantity of iodine represents the iodine used in oxidizing the sulphur dioxide. The strength of the sulphur dioxide solution may then be calculated according to the formula:



EFFECT OF METALLIC IRON.

As all mill samples and laboratory samples prepared in the ordinary way contain appreciable quantities of metallic iron, the effect of such iron was carefully investigated. Samples were prepared from various representative commercial ores in the following manner: Selected lumps, washed to remove any adhering particles of metallic iron, were pulverized in Wedgwood mortars. Equal portions of these samples were weighed out and adulterated with different known quantities of iron filings. Table 2 shows the results of one series of these tests.

TABLE 2.—*Oxidized copper reported by sulphur dioxide method on samples containing 0.25 per cent to 3 per cent of iron filings.*

Percentage of iron added.	Percentage of oxidized copper.				
	Ore No. 1.	Ore No. 2.	Ore No. 3.	Ore No. 4.	Ore No. 5.
None.	0.38	0.80	2.10	3.40	4.12
0.25	0.38	0.82	2.11	3.42	4.11
0.50	0.37	0.82	2.12	3.44	4.13
1.00	0.37	0.81	2.10	3.40	4.12
2.00	0.37	0.81	2.08	3.36	4.10
3.00	0.36	0.75	1.98	3.10	3.84

With 2 per cent or less of metallic iron the results are constant, but when more is present the results are unreliable. Mill products obtained under all sorts of crushing conditions have come to the laboratory of the Tucson station and, after being bucked down on a soft bucking plate with a soft muller, the resulting samples have invariably contained less than 1 per cent metallic iron.

An essential requirement is the continued presence of a strong excess of SO_2 , which readily dissolves the metallic iron. In order to insure this excess, the SO_2 must be introduced in the form of sulphur dioxide solution. If SO_2 is introduced in the form of a gas, unstable conditions arise from the unequal distribution of the gas; then the presence of metallic iron in quantities much less than 2 per cent may cause the precipitation of copper in the form of cement copper, cupro-cupric sulphites, and probably also as complex sulphides which are not redissolved.

COMPARISON WITH OTHER METHODS.

Comparative results obtained with the four methods described on ores and mill products from the Morenci, Globe, Ray, and Ajo districts in Arizona, from Chino, N. Mex., from Bingham, Utah, and from Ely, Nev., are presented in Table 3. The table shows that, compared with the sulphur dioxide method, the results for oxidized copper are high with the sulphuric acid method and low with the ammonia method. The sodium-tartrate method uniformly shows returns slightly lower. The last sample in the table, designated "Miami ore (special test)," was crushed to 20-mesh size, special care being taken to prevent overcrushing. Five portions were then taken and crushed with the same care to the successive sizes listed. The uniformity of results for oxidized copper by the sulphur dioxide method is evident. The results with the sodium-tartrate method, which was developed on this class of ore, show more variation and are slightly lower. The sulphuric acid method shows high returns, which are progressively higher for the finer sizes. Results with the ammonia method are low and show considerable variation.

TABLE 3.—Results with the four methods compared.

Source of sample.	Copper content.	Oxidized copper (oxide, carbonate, and silicate).			
		By sulphur dioxide method.	By sodium tartrate method.	By sulphuric acid method.	By ammonia method.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Inspiration mill feed.....	1.31	0.35	0.33	0.41	0.36
Inspiration mill slimes.....	.43	.32	.28	.35	.07
Miami complex ore.....	2.24	1.05	1.02	1.32	.91
Morenci mill sands.....	.64	.09	.07	.23	.09
Morenci mill slimes.....	.52	.20	.18	.26	.04
Ray mill sands.....	.47	.04	.03	.18	.12
Ray mill slimes.....	.52	.27	.25	.32	.22
Chino mill heads.....	1.18	.19	.19	.52	.24
Chino mill tails.....	.45	.13	.15	.31	.02
Chino mine ore.....	2.49	.95	.94	1.18	1.12
New Cornelia (Ajo) ore.....	1.26	.42	.42	.76	.22
Ruth mill heads.....	1.65	.25	.29	.41	.49
Giroux mill tails.....	.58	.01	.02	.08	.04
Nevada Consolidated mill heads.....	.82	.07	.05	.30	.25
Nevada Consolidated mill tails.....	.33	.02	.03	.08	.04
Utah Copper mine ore.....	2.53	.24	.26	.57	.50
Utah Copper mill feed.....	.89	.60	.56	.63	.37
Utah Copper mill tails.....	.63	.07	.06	.11	.09
Miami ore (special test):					
20-mesh.....	2.25	1.06	.96	1.18	0.83 to .90
48-mesh.....	2.25	1.05	.98	1.28	.62 to .98
65-mesh.....	2.25	1.06	1.00	1.30	.95 to 1.10
100-mesh.....	2.25	1.06	.97	1.32	.91 to 1.10
150-mesh.....	2.25	1.07	.92	1.32	.92 to 1.06
200-mesh.....	2.25	1.06	1.02	1.34	.88 to 1.09

NOTE.—In the sulphur dioxide method any finely divided metallic copper that passed through the screen in the preparation of the sample would be reported as oxidized copper. In the other three methods metallic copper would be reported as sulphide.

CONCLUSIONS.

Enough work has been done with the sulphur dioxide method to substantiate the following claims:

1. Cuprite, melaconite, malachite, azurite, chrysocolla, and fine metallic copper are dissolved rapidly and completely.

2. Chalcocite and chalcopyrite are not affected.

3. Metallic iron in ordinary quantities, even up to 2 per cent, dissolves rapidly and has no effect on the determination, provided there is a strong excess of SO_2 , introduced as SO_2 solution.

4. There is no gelatinization of silica, and the possible loss of copper from this cause, noted in analyses by the other methods described, is eliminated.

5. The method is applicable alike to high-grade and to low-grade ores. The manipulation is simple and the possible sources of error are few. One chemist can keep a 6-unit electrolytic outfit working to full capacity on porphyry ores.

6. Crushing fine enough to liberate completely the mineral particles is essential. Ores containing an appreciable proportion of chrysocolla should always be pulverized to 150 mesh.

7. Any metallic copper present, as flakes or large particles would, of course, be removed during the preparation of the sample and treated as scales. Fine metallic copper remaining in the pulverized sample would be dissolved and reported with the metallic copper. If a separate determination of metallic copper is considered necessary, this can be made by amalgamation, preferably in an amalgamated copper pan.

APPENDIX.

The statement on page 2 that chalcopyrite, bornite, and chalcocite are more or less soluble in dilute sulphuric acid was based on a series of experiments with selected specimens of these minerals. Although these showed no oxidation even under the microscope, any oxidized copper that might have been present was removed by a preliminary treatment. In this treatment parallel tests were made with the SO₂, Miami, sulphuric acid, and ammonia processes. After such preliminary treatment the samples of the selected minerals mentioned above were subjected to the treatment already outlined in this paper. These results plainly show that the decomposition of the sulphide ores increases with the time of contact and the fineness of ore.

A picked specimen of pure chalcocite was ground in a porcelain mortar to pass 100 mesh. A 2-gram sample of the fine chalcocite was successively treated four times with 100 c. c. of 4 per cent sulphuric acid by bottle rolling for two hours, with the results shown in Table 2, page 9.

Hence chalcocite is partly soluble in H₂SO₄ and the rate of solubility is almost proportional to the time of contact.

The experiments bearing on the solubility of copper silicates in SO₂ covered a wide range, including ore from all the big "porphyry" mines; the results show that copper in copper silicates is entirely soluble in SO₂. Specimen samples of chrysocolla and also selected samples of copper silicates from various mines in the Southwest showed, by the analytical method of the author, that all the copper was soluble in SO₂, none remaining in the treated residue. This work also shows that the more resistant silicates give up their copper much more readily in SO₂ than in an equal strength of sulphuric acid.

Where metallic copper appears in flakes or large particles, the accepted practice in sampling, removing and calculating this metallic copper separately, must be followed.

SO₂ precipitates copper from sulphate solution under heat and high pressure. The Weidlein method, as given under United States Patent No. 1223454, specifies a temperature of 150° C. and a pressure of 100 pounds per square inch.

The author's conditions are entirely different, requiring no heat and only such small pressure as a 3 per cent SO₂ solution may form with the air in the bottle to produce an equilibrium between the gas and the solution.

Metallic iron in quantity affects the results, but with the procedure outlined and with ores as usually prepared for a sample, there is no apparent error. This statement is based on a number of experiments with different commercial ores. Selected lumps known to be free from metallic iron were crushed in a Wedgewood mortar and to this iron-free sample varying quantities of iron filings were added, all giving practically the same results up to 2 per cent metallic iron. When the iron content exceeds 2 per cent the resulting error increases rapidly, particularly when the SO_2 is introduced as a gas. The unstable condition caused by a varying excess of SO_2 throughout the dissolving results in part of the copper being thrown out or precipitated as metallic copper, cupro-cupric sulphites and, probably, complex sulphides. By using a large excess of SO_2 in solution, metallic copper or cupro-cupric sulphites are not thrown down, even though several per cent of metallic iron may be present; also the amount of complex precipitates is much less than when the SO_2 is introduced as a gas. The use of sulphurous acid solution is specified because it insures an excess of SO_2 at all times and permits simple and convenient manipulation. Of course, if the pulp sample carries much metallic iron this must be removed with a magnet before analysis. Ores as regularly prepared for a sample contain only a negligible amount of metallic iron and this does not affect the result.

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